allowing the Ba-coordinating O atoms some freedom of movement from the ideal positions to accommodate both the tetrahedral symmetry of the perbromate ion and the hydrogen bonding of the water molecules.

The barium perbromate trihydrate structure appears to be isomorphic with the structure of barium perchlorate trihydrate as determined by Mani & Ramaseshan (1960), although these authors could not decide on the basis of their data whether the space group was $P6_3$ or $P6_3/m$. The average Ba—O distance is 3·035 (5) Å in the perchlorate structure, somewhat larger than the corresponding distance in the present structure.

In the same vein, it is interesting to note that each of the perbromate salt structures which has been reported (Ba, NH_4, K, Cs and Rb) is isomorphic with the corresponding perchlorate salt structure.

Thermogravimetric and differential thermal analysis data obtained by Isupov, Gavrilov & Kirin (1977) have been interpreted as demonstrating the existence of a barium perbromate tetrahydrate salt. Since there is insufficient space to accommodate another water molecule in the trihydrate structure, barium perbromate tetrahydrate must crystallize in a different space group.

The support of WJR by an Ohio State University Presidential Fellowship and the partial support by a Thesis Parts Appointment at Argonne National Laboratory are acknowledged with pleasure. EHA acknowledges support from the Office of Basic Energy Sciences, Division of Chemical Sciences, US Department of Energy. We thank Dr J. C. Gallucci for numerous helpful discussions. Computational facilities were provided by The Ohio State University IRCC.

References

Appelman, E. H. (1968). *J. Am. Chem. Soc.* **90**, 1900–1901.

Appelman, E. H. (1972). *Inorg. Synth.* **13**, 1–9.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Gebert, E., Peterson, S. W., Reis, A. H. & Appelman, E. H. (1981). *J. Inorg. Nucl. Chem.* **43**, 3085–3089.

Gebert, E., Peterson, S. W., Reis, A. H. & Appelman, E. H. (1982). *Polyhedron*, **1**, 567.

Gerkin, R. E. & Reppart, W. J. (1987). *Acta Cryst.* C**43**, 623–631.

International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Isupov, V. K., Gavrilov, V. V. & Kirin, I. S. (1977). *Zh. Neorg. Khim.* **22**, 2592–2594.

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Mani, N. V. & Ramaseshan, S. (1960). *Z. Kristallogr.* **114**, 200–214.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Siegel, S., Tani, B. & Appelman, E. (1969). *Inorg. Chem.* **8**, 1190–1191.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. W. & Hall, S. R. (1972). The *XRAY* system–version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.

Tutov, A. G., Gavrilov, V. V., Isupov, V. K., Kolycheva, T. I. & Fundamenskii, V. S. (1986). *Zh. Neorg. Khim.* **31**, 589–592.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1988). C**44**, 962–965

Structure of Calcium Zinc Tetrabromide Pentahydrate

By Rumen Duhlev,* I. David Brown and Romolo Faggiani

Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1

(*Received* 19 *January* 1988; *accepted* 15 *February* 1988)

Abstract. $CaZnBr_4.5H_2O$, $M_r = 515·15$, triclinic, $P\bar{1}$ {Hall symbol $\bar{P}1$ [*Acta Cryst.* (1981), A**37**, 517–525]}, $a = 7·472$ (2), $b = 9·722$ (3), $c = 10·020$ (3) Å, $\alpha = 84·67$ (2), $\beta = 113·43$ (2), $\gamma = 112·38$ (2)°, $V = 616·1$ (3) Å^3, $Z = 2$, $D_x = 2·78$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 15·03$ mm^{-1}, $F(000) = 480$, room temperature, $R = 0·049$ ($wR = 0·044$) for 1630 unique reflections. The structure consists of centrosymmetric dimeric rings $[Ca(H_2O)_5ZnBr_4]_2$ with Zn tetrahedrally coordinated by four Br atoms ($\langle$Zn—Br$\rangle$ = 2·41 Å) and Ca sevenfold coordinated by five O_w ($\langle$Ca—O$\rangle$ = 2·37 Å) and two Br ($\langle$Ca—Br$\rangle$ = 3·11 Å) from two different $ZnBr_4$ groups. The rings are held together by O—H···Br and O—H···O hydrogen bonds.

Introduction. Duhlev & Balarew (1986) reported two new double salts, $CaZnBr_4.8H_2O$ and $CaZn_2Br_6.6H_2O$, in their study of the phase equilibrium in the system $CaBr_2$–$ZnBr_2$–H_2O at 298 K. In an attempt to

---

* On leave from the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria.

0108-2701/88/060962-04$03.00

Table 1. *Atomic positions and equivalent isotropic atomic displacement factors* (Å^2)

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ or U_{iso} (for H atoms).

	x	y	z	U_{eq}
Zn	0·11811 (16)	0·72577 (11)	0·26705 (11)	0·0243
Br(1)	0·24257 (15)	0·70816 (11)	0·08128 (10)	0·0328
Br(2)	0·24091 (15)	0·99208 (10)	0·32686 (10)	0·0286
Br(3)	0·29967 (17)	0·61493 (11)	0·47212 (10)	0·0347
Br(4)	−0·25621 (15)	0·62119 (10)	0·16895 (11)	0·0319
Ca	−0·0784 (3)	0·1468 (2)	0·2118 (2)	0·0262
O(1)	0·2256 (11)	0·3383 (8)	0·1998 (8)	0·042
O(2)	0·0916 (11)	0·2357 (7)	0·4610 (7)	0·039
O(3)	−0·2870 (10)	−0·0481 (7)	0·3183 (7)	0·033
O(4)	−0·2938 (13)	0·2642 (8)	0·2254 (8)	0·060
O(5)	−0·2463 (12)	−0·0488 (7)	0·0292 (7)	0·043
H(11)	0·3523	0·3462	0·3163	0·08
H(12)	0·2091	0·3949	0·1546	0·08
H(21)	0·2020	0·3527	0·5222	0·08
H(22)	0·1877	0·2017	0·5320	0·08
H(31)	−0·4005	−0·1601	0·2805	0·08
H(32)	−0·3082	−0·0391	0·3951	0·08
H(41)	−0·2681	0·3597	0·1818	0·08
H(42)	−0·3005	0·2799	0·2805	0·08
H(51)	−0·2747	−0·1730	0·0555	0·08
H(52)	−0·2276	−0·0311	−0·0477	0·08

obtain crystals of $CaZnBr_4.8H_2O$, a sample of a saturated aqueous solution containing $CaBr_2$ and $ZnBr_2$ in a molar ratio 1:1·2 was left in a desiccator under vacuum for several weeks until its contents solidified into a hard glass-like colourless mass. A crystal was selected from this mass and during the course of the structure determination it became clear that its composition was $CaZnBr_4.5H_2O$, indicating that at least some of the original $CaZnBr_4.8H_2O$ crystals had been dehydrated to $CaZnBr_4.5H_2O$.

Experimental. A cylindrical extremely hygroscopic crystal with diameter 0·23 and length 0·27 mm was sealed in a thin-walled capillary under dry nitrogen and mounted on a Syntex $P2_1$ diffractometer. Unit-cell parameters were determined from 15 well centred strong reflections in the range $17 < 2\theta < 25°$. Intensities were measured at 298 K for 1857 reflections with $0 \le h \le 8$, $-10 \le k \le 9$, $-10 \le l \le 9$, $2\theta < 45°$ and were corrected for Lorentz and polarization effects. No correction was made for absorption since application of a ψ-scan absorption correction neither improved the agreement index nor significantly changed the refined parameters. The intensities of the $04\bar{3}$ and $\bar{2}1\bar{2}$ reflections were monitored after every 50 measurements and showed variations of less than 1·9%. The symmetry-equivalent reflections were averaged (R_{int} = 0·008) to give 1630 unique reflections, all of which were used in the structure solution and refinement. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986). The scale factor, extinction coefficient and all variable (non-hydrogen) positional and displacement parameters were refined by least squares [function minimized = $\sum w(|F_o| - |F_c|)^2$] with *SHELX*76 (Sheldrick, 1976). The positions of the H atoms were found from the difference map close to the positions where they were expected. The final refinement was performed with fixed H positions and H atomic displacement parameters fixed at 0·08 Å^2. Weights used were $w^{-1} = \sigma^2(F_o) + kF_o^2$ where $\sigma(F_o)$ is the error derived from counting statistics and k was set at 0·0007, a value which minimized the variation of $\langle w\Delta^2\rangle$ with $|F_o|$. The final R = 0·049, wR = 0·044 and goodness of fit S = 1·26 [R = 0·037, wR = 0·037 and S = 1·34 when 356 reflections with $I < 3\sigma(I)$ were omitted]. The final average shift/e.s.d. = 0·001 (max. = 0·002). The largest negative peak in the final difference electron density map is −0·77 e Å^{-3} and the largest positive peaks (found between 1·15 and 1·44 Å from the centres of the Br atoms) are +0·97 (10) e Å^{-3}. The secondary-extinction coefficient (Larson, 1967) g = 0·0094 (2). Complex atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates are given in Table 1.*

Discussion. Using the procedure suggested by Balarew & Duhlev (1984), one can predict that the four Br atoms will tetrahedrally coordinate the Zn while the five oxygens from water molecules will bond to calcium. This is exactly what is observed, with the coordination

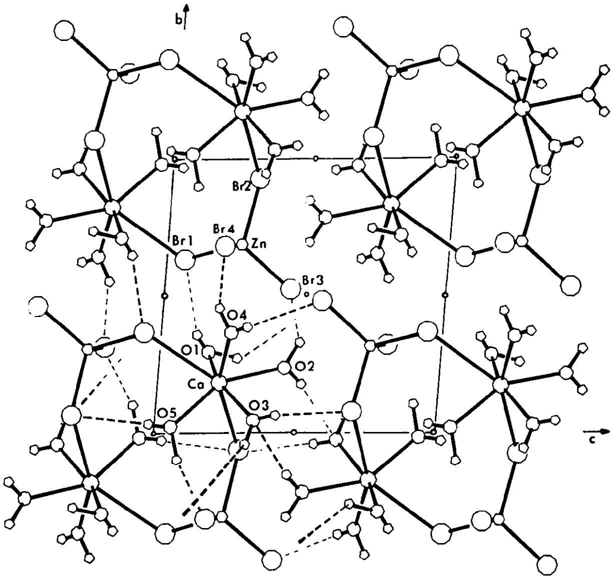

Fig. 1. Projection of the crystal structure of $CaZnBr_4.5H_2O$ in the *bc* plane viewed almost along the *a* axis. The hydrogen bonds stronger than 0·08 v.u. are shown.

---

* Lists of structure factors and anisotropic atomic displacement factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44775 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and angles* (°)

Polyhedron $Ca(H_2O)_5Br_2$

Ca	O(1)	O(2)	O(3)	O(4)	O(5)	Br(1^{i})	Br(2^{ii})
O(1)	2·365 (7)	3·111 (10)		3·778 (14)	3·876 (13)	3·402 (7)	3·513 (8)
O(2)	82·0 (3)	2·374 (7)	3·038 (8)	3·004 (10)			3·529 (9)
O(3)	157·3 (2)	78·6 (2)	2·420 (7)	3·105 (11)	3·032 (12)		
O(4)	106·5 (3)	78·9 (3)	81·2 (3)	2·349 (7)	3·968 (13)	3·220 (9)	
O(5)	114·8 (3)	150·9 (3)	78·8 (3)	115·0 (3)	2·354 (7)	3·387 (7)	3·576 (7)
Br(1)	75·00 (17)	133·85 (20)	127·15 (16)	70·29 (19)	74·72 (18)	3·130 (2)	
Br(2)	79·0 (2)	79·4 (2)	85·8 (2)	156·51 (19)	81·0 (2)	132·31 (9)	3·083 (2)

Tetrahedron $ZnBr_4$

Zn	Br(1)	Br(2)	Br(3)	Br(4)
Br(1)	2·4323 (19)	3·871 (2)	3·8271 (18)	3·930 (2)
Br(2)	105·20 (6)	2·4385 (16)	3·9347 (19)	3·9357 (19)
Br(3)	105·00 (7)	109·10 (5)	2·3893 (16)	4·0752 (19)
Br(4)	109·47 (6)	109·50 (7)	117·39 (6)	2·3783 (16)

Hydrogen bonds and angles

O—H···*X*	O—H	H···*X*	O···*X*	O—H···*X*	H—O—H
O(1)—H(11)···Br(3^{iii})	1·16	2·53	3·657 (6)	163	129
O(1)—H(11)···Br(3)	1·16	3·38	3·743 (9)	99	
O(1)—H(12)···Br(1)	0·70	3·00	3·652 (8)	156	
*O(1)—H(12)···Br(4^{i})	0·70	3·42	3·768 (8)	115	
O(2)—H(21)···Br(3)	1·17	2·43	3·405 (7)	139	85
O(2)—H(21)···Br(4^{iii})	1·17	2·98	3·637 (7)	115	
O(2)—H(22)···O(3^{iv})	0·93	2·14	3·010 (10)	156	
O(2)—H(22)···Br(4^{iii})	0·93	3·36	3·637 (7)	100	
O(3)—H(31)···Br(1^{v})	1·08	2·53	3·417 (5)	139	98
*O(3)—H(31)···Br(4^{ii})	1·08	3·17	3·790 (8)	117	
O(3)—H(32)···Br(2^{iii})	0·86	2·68	3·507 (8)	161	
O(4)—H(41)···Br(4)	0·97	2·50	3·385 (8)	151	101
O(4)—H(42)···Br(3^{iii})	0·61	2·77	3·372 (9)	173	
O(4)—H(42)···Br(4)	0·61	3·34	3·385 (8)	89	
*O(5)—H(51)···Br(4^{ii})	1·17	2·23	3·365 (7)	163	111
*O(5)—H(52)···Br(2^{i})	0·83	2·75	3·573 (8)	170	

Symmetry code: (i) $-x, 1-y, -z$; (ii) $x, y-1, z$; (iii) $-x, 1-y, 1-z$; (iv) $-x, -y, 1-z$; (v) $x-1, y-1, z$.

* Hydrogen bonds formed within the dimer.

Table 3. *Bond valences*

	Br(1)	Br(2)	Br(3)	Br(4)	O(1)	O(2)	O(3)	O(4)	O(5)	Sum
Zn	0·44	0·43	0·50	0·51						1·88
Ca	0·17	0·19			0·34	0·33	0·29	0·36	0·36	2·03
H(11)			0·09 0·03		0·89					1·00*
H(12)	0·08			0·02	0·90					1·00*
H(21)			0·12	0·05		0·83				1·00*
H(22)				0·03		0·87	0·10			1·00*
H(31)	0·11			0·04			0·85			1·00*
H(32)		0·12					0·88			1·00*
H(41)				0·16				0·84		1·00*
H(42)			0·17	0·03				0·80		1·00*
H(51)				0·16					0·84	1·00*
H(52)		0·11							0·89	1·00*
Sum	0·80	0·85	0·91	1·00	2·13	2·03	2·12	2·00	2·08	

* The valences of the O—H bonds were chosen to ensure that the valence sums around H are 1·00.

environment around Ca completed by two Br atoms shared with two different $ZnBr_4$.

$[Ca(H_2O)_5ZnBr_4]_2$ dimers form rings around the centre of symmetry at the origin (Fig. 1). The bond distances and angles are shown in Table 2. All of them are within the normal ranges observed in similar compounds. The two Ca—Br distances are longer than the sum of the ionic radii (2·95 Å) since the bromines are much more strongly bonded to Zn than to Ca, as can be seen from the bond valences (Table 3) calculated with the bond length/bond valence parameters of Brown & Altermatt (1985). In calculating the valences of the hydrogen bonds in this table H atoms were assumed to lie along the observed O—H bond at a distance of 0·96 Å from O. The bond valence sums around each atom agree satisfactorily with the atomic valences. The strongest bonds in the structure are the O—H bonds (0·80–0·90 v.u.), followed by the Zn—Br bonds: two stronger ones to the terminal Br(3) and Br(4) (0·50–0·51 v.u.) and two weaker to the bridging Br(1) and Br(2) (0·43–0·44 v.u.). The Ca—O bond strengths vary between 0·29 and 0·36 v.u. with the weak bond [Ca—O(3) = 2·420 Å] being to the only oxygen that acts as a hydrogen-bond acceptor. The two Ca—Br (bridging) bonds are comparable in strength (0·17–0·19 v.u.) to the strongest H bonds. Each H atom forms one moderately strong hydrogen bond (0·08–0·17 v.u., angles O—H···Br or O—H···O greater than 135°) and most of the H atoms show in addition weaker interactions (≤ 0·05 v.u., angles O—H···Br less than 135°). The hydrogen-bond scheme is described in Table 2 and shown in Fig. 1.

Although the pentahydrate $CaZnBr_4.5H_2O$ does not appear as an equilibrium solid phase in the Ca-

Br_2–$ZnBr_2$–H_2O system at 298 K (Duhlev & Balarew, 1986), the corresponding chloride, $CaZnCl_4.5H_2O$, is the only double salt reported in the $CaCl_2$–$ZnCl_2$–H_2O system at 298 K (Hudgins, 1964). We expect the chloride compound to be built of the same structural motifs, packed in a similar if not the same way. Another compound with the same formula type, $MgZnCl_4.5H_2O$, has been reported (Balarew & Spassov, 1980) but because of the large difference in size between Mg^{2+} and Ca^{2+}, the environment around Mg^{2+} is expected to be different from that of Ca^{2+} in the present structure.

We wish to thank the Natural Science and Engineering Research Council of Canada for an operating grant to one of us (IDB).

References

Balarew, Chr. & Duhlev, R. (1984). *J. Solid State Chem.* **55**, 1–6.

Balarew, Chr. & Spassov, D. (1980). *Russ. J. Inorg. Chem.* **25**, 1551–1556.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Duhlev, R. & Balarew, Chr. (1986). *Rev. Chim. Miner.* **23**, 116–124.

Hall, S. R. (1981). *Acta Cryst.* A**37**, 517–525.

Hudgins, C. M. (1964). *J. Chem. Eng. Data.* **9**, 434–435.

International Tables for X-ray Crystallography (1974). Vol. IV, Tables 2.2B and 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS86*. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.

Acta Cryst. (1988). C**44**, 965–967

Structures of $Rb_2[InCl_5(H_2O)]$ and $Cs_2[InCl_5(H_2O)]$

By Xavier Solans

Depto de Cristalografía, Universidad de Barcelona, Gran Via 585, 08007 Barcelona, Spain

and Mary C. Moron and Fernando Palacio

Instituto de Ciencia de Materiales de Aragón, CSIC y Univ. de Zaragoza, 50009 Zaragoza, Spain

(*Received 22 July 1987; accepted 1 February 1988*)

Abstract. (I) Rubidium aquapentachloroindate, $Rb_2[InCl_5(H_2O)]$, $M_r = 481{\cdot}04$, orthorhombic, *Pnma*, $a = 14{\cdot}050\,(3)$, $b = 10{\cdot}087\,(2)$, $c = 7{\cdot}215\,(2)$ Å, $D_x = 3{\cdot}124$ g cm^{-3}, $Z = 4$, $V = 1022{\cdot}5\,(7)$ Å^3, $F(000) = 872$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 135{\cdot}01$ cm^{-1}, $T = 288$ K. Final $R = 0{\cdot}021$ for 764 reflections. (II) Caesium aquapentachloroindate, $Cs_2[InCl_5(H_2O)]$, $M_r = 575{\cdot}91$, orthorhombic, *Pnma*, $a = 14{\cdot}410\,(3)$, $b = 10{\cdot}382\,(2)$, $c = 7{\cdot}416\,(1)$ Å, $D_x = 3{\cdot}447$ g cm^{-3}, $Z = 4$, $V = 1109{\cdot}5\,(3)$ Å^{-3}, $F(000) = 1016$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 98{\cdot}06$ cm^{-1}, $T = 288$ K. Final $R = 0{\cdot}020$ for 765 reflections. In both compounds the anions are distorted octahedra, with In, O and three Cl atoms on the mirror plane. Cl···O ($-x, -y, 2-z$) distances of 3·148 (9) (I) and 3·09 Å (II) indicate hydrogen bonding between O and Cl atoms of neighbouring octahedra. All other bond lengths are normal. Comparison of both structures with related $A_2[MX_5(H_2O)]$ structures is also made.

Introduction. The series of compounds $A_2[InCl_5(H_2O)]$, where $A = NH_4$, K, Rb, Cs, are of interest because they are the diamagnetic analogues of the intensively studied series of antiferromagnets $A_2[FeCl_5(H_2O)]$ (Carlin & Palacio, 1985). In fact, all the compounds in both series whose structures are known are orthorhombic, although they are not all isomorphic. The Cs/Fe compound belongs to the space group *Cmcm* (O'Connor, Deaver & Sinn, 1979; Greedan, Hewitt, Faggiani & Brown, 1980) and is isomorphic to the analogous ruthenium(III) material (Hopkins, Zalkin, Templeton & Adamson, 1966). The remaining compounds belong to space group *Pnma* (Carlin, Bhatia & O'Connor, 1977) and therefore the K and NH_4 derivatives of the Fe and In compounds are isomorphic (Lindqvist, 1947; Bellanca, 1948; Klug, Kummer & Alexander, 1948; Wignacourt, Mairesse & Barbier, 1976; Figgis, Raston, Sharma & White, 1978).

We report here on the crystal structures of both the Cs and Rb derivatives of the In series. Our aim was to elucidate whether $Cs_2[InCl_5(H_2O)]$ would follow the tendency of its Fe and Ru analogues or would belong to the much wider family of isomorphic compounds with space group *Pnma*. In addition, since $Rb_2[FeCl_5(H_2O)]$ is very interesting from a magnetic point of view

0108-2701/88/060965-03$03.00